

Conditions that Favor Tar Production from Pyrolysis of Large, Moist Wood Particles

Marcia Kelbon, Scott Bousman, and Barbara Krieger-Brockett

Dept. of Chemical Engineering, BF-10
University of Washington
Seattle, WA 98195

Abstract

The production of pyrolytic oils from biomass will be greatly facilitated if large, and perhaps moist, particles can be used directly as a feedstock. This paper describes experiments to quantify product evolution rates, as well as spatial and temporal temperature distributions, during pyrolysis of large wood particles. The experiments have been performed using well-defined, reactor-independent conditions which will aid in identifying favorable conditions for tar production from large particles. The experiments reveal that an optimum moisture content can facilitate tar production. The reacted fraction that is tar is greater for intermediate moisture contents, particle sizes, and heating rates, and the optimum tar production conditions for moist feed change with both heating intensity and particle size.

INTRODUCTION

The economics of making pyrolytic oils from biomass will be improved if large, and perhaps moist, particles can be used directly as a feedstock. This is a result of the high cost of size reduction and drying of fibrous and often green biomass. However, the pyrolysis of realistically sized particles (about 1 x 1 x .5 cm or greater) is complicated by the lack of uniform temperature profiles within the particle, and the synergistic effects that external heating intensity, moisture, and particle size have in altering the intraparticle temperature histories. Nevertheless, both present and planned industrial biomass converters employ large particles, sometimes using them in fluidized beds which are less sensitive to feed size distributions (1).

Selectively producing a particular pyrolysis fraction such as tar, or specific components in any fraction, is difficult. The majority of studies to date have used finely ground (< 100 μm diameter) wood samples in which heat transfer rates are rapid enough to cause a uniform particle temperature, and mass transfer is fast enough to minimize secondary reactions. For these particles, pyrolysis with a high heating rate to moderately high temperatures generally favors tar formation, if the tar can be quickly removed from the reaction zone. However, reducing fibrous materials to such a small size is costly. Pyrolysis feeds are likely to be wood chips used routinely in the forest products industry. In wood chip pyrolysis, the particle interior heats slowly and secondary reactions of tar are significant.

The scope of this preprint is limited to the presentation and discussion of experimental conditions of practical importance that maximize tar from pyrolysis of large wood particles. By design, results are as independent of reactor type to the greatest possible, and reveal the effects of heat and mass transport that are critical to conversion of the large, poorly conducting porous particles. Since typical feeds are heterogeneous, the entity appropriate for chemical engineering studies is the single particle. The findings are then applicable to all reactors in which the chosen experimental conditions prevail. The study of reacting single particles has proven extremely successful in the development of catalytic reactors (2) and coal pyrolysis (3,4,5).

Since reaction temperature is not an independent variable for large pyrolyzing particles, special attention must be given to choosing experimental conditions for the 0.5 cm to 1.5 cm thick

particles studied. Heating intensity can be made precise by controlling the applied heat flux at the particle surface or imposing a surface temperature, and measuring the particle thermal properties (6). One dimensional heating has been used experimentally (7,8) and typifies the type of heat transfer experienced by most wood chips owing to the large aspect ratios they usually have (9). The lowest heating intensity studied, $2 \text{ cal/cm}^2\text{-s}$, barely chars thick samples (or causes smoldering combustion if oxygen is present). The highest, $6 \text{ cal/cm}^2\text{-s}$, is found in furnaces or high temperature reactors designed for maximum heating of particles. Biomass moisture varies with species and age as well as from region to region. Typical moisture contents (dry basis) found for feed piles in the Pacific Northwest range from 10% to 110%, thus the choices for the experiments reported here. A more complete discussion of practical conditions appears elsewhere (10). Also, simultaneous variations in two or three experimental conditions were systematically investigated in order to determine if pyrolysis tar yields, as well as other reaction products, were dependent on process condition combinations in a non-additive, or multiplicative way (11).

EXPERIMENTAL

Apparatus - A description and diagram of the single particle pyrolysis reactor appears in Chan, et al. (12) but a brief presentation is given for completeness. A wood cylinder was placed in a glass sleeve and reactor assembly. An arc lamp provided radiative, spatially uniform, 1-D axial heating as verified by absolute calibration of the heat flux (6,13, 14). The heating period was the same for all experiments, 12 min, sufficiently short to enable the study of active devolatilization in the thinnest of these particles. Thermocouples at 2, 4, and 6 cm from the heated face automatically measured the devolatilization front progress. An infrared pyrometer, mounted off-axis from the arc lamp beam, measured the surface temperature of the pellet. The glass housing and baffle allowed the front face of the pellet to be uniformly irradiated and prevented volatiles from condensing on the window. The large helium carrier gas flowrate quenched the volatiles and swept them without significant backmixing or reaction (6) to the analysis system. The helium pressure on the unheated face was slightly elevated to ensure volatiles flow toward the heated face for maximum recovery. It has been verified (7) that during devolatilization of a large particle, nearly of the volatiles flow toward the heated surface owing to the decreased porosity behind the reaction front. A cold trap (packed with glass wool and at -40°C) immediately downstream from the reactor condensed tars and water from the volatiles. Permanent gases were sampled near the cold trap exit at preselected times during the experiment using two automated gas sampling valves, thus providing information on evolution rates of gaseous products. All volatiles were later analyzed by gas chromatography.

Sample Preparation - The wood pellets were all cut, with great attention to grain direction, from uniform sections of the same lodge pole pine tree provided by Weyerhaeuser Co. (Corvallis Mill). The cylinders were oven-dried at 90°C for at least three weeks. Moisture was quantitatively added using a microsyringe and balance, and allowed to come to a uniform distribution as described by Kelbon (13).

Gas Analysis - Permanent gases, operationally defined as all components passing through the -40°C cold trap, were collected in 30 stainless steel sample loops of known volume. Immediately after the experiment, samples were automatically injected into a Perkin-Elmer Sigma 2 Gas Chromatograph using a Supelco 100/120 mesh Carbosieve S column 1/8 in. diameter and 5 ft. long. The peaks were integrated and identified by a Perkin-Elmer Sigma 15 Chromatography Data Station. Both a thermal conductivity detector and a flame ionization detector were used as described in Bousman (14).

Tar Analysis - The tar is comprised of two parts, that which was trapped and that which was washed from the reactor, though the latter is often a small amount. The tar trap sample was analyzed for water and low molecular weight tar compounds by gas chromatography using a Supelco 80/100 mesh Porapak Q column 1/8 in. diameter and 1.5 ft long. After the low molecular weight tar analysis, the trap tar and reactor tar samples were treated with approximately 2 g of MgSO_4 to remove water and then filtered. A known quantity of p-bromophenol was added to each sample as an internal standard. Each sample was concentrated in order to remove THF while minimizing the loss of the other compounds. The resulting high molecular weight tar liquid was analyzed by gas chromatography using either a J and W Scientific DBWAX or Carbowax 20M fused silica capillary column 0.25 mm ID, 30 m long with a Perkin-Elmer splitting injection port. The major peaks which appeared in the

majority of the samples are numbered and presented in this paper as simplified, composite chromatograms.

Char Analysis - The char was weighed and a qualitative chemical analysis of some char samples was performed using a Fourier Transform Infrared Spectrometer (FTIRS) with preparation as described in Bousman (14). The surface area of the char was also characterized using CO₂ adsorption.

Experimental Design - The experimental conditions were picked according to a type of factorial experimental design which facilitates identification of optima and empirical models of the class given in Eq. 1 (11,15):

$$y_k = b_0 + \sum b_i x_i + \sum \sum b_{ij} x_i x_j, \quad \text{for } i \leq j, \quad (1)$$

where

y_k is the k-th product yield of interest,

x_i, x_j are the independent variables (process controllables) and

b_0, b_i and b_{ij} are least square parameter estimates obtained from multiple regression.

When variables combine to affect the reaction process in a non-additive way, as when the last term of Eq. 1 is large, non-linear dependence of yields on the process controllables is demonstrated. Plots of Eq. 1 are presented in subsequent figures as trend lines.

RESULTS AND DISCUSSION

The range of intraparticle temperatures measured throughout pyrolysis at a constant heat flux of 4 cal/cm²-s for a particle initially at 60% moisture (Fig. 1) corresponds to those found in other studies for both small (16-18) and large (19) particles. As can be seen when moisture is added, the temperature rises in the first ~30 sec to a plateau at 100 C until the water has locally evaporated, and then the temperature rises to the same level as found in dry wood particles, although at a somewhat later time. The surface temperature is of some qualitative value but once volatiles are produced, the infrared pyrometer cannot accurately "see" the surface and the measured temperature is artificially low. Note that reaction in zones near the surface experience quite high heating rates, which should favor tar production early in the devolatilization of a large particle.

In this preprint, overall yields are reported as graphs rather than tables, and correspond to time-integrated pyrolysis or devolatilization products from a large wood particle heated under constant applied heat flux at the surface. The yields are expressed as weight fractions of that which reacted in the 12 min pyrolysis duration. Fractional yields are an important measure of selectivity and are useful for downstream separation process considerations. The appropriate measure of experimental reproducibility and accuracy is the standard error calculated from replicate runs. This is given as an uncertainty. However, because of the inherent difficulty in recovering all products, especially tars, the mass balances do not always add to 100%. Thus, another measure of error is the discrepancy in the mass balance. For these experiments, the average mass balance closure was 80%, with a standard deviation of 11%.

In Fig. 2 the weight fraction water-free tar produced from the fixed duration pyrolysis of dry wood particles of several thicknesses is presented. The symbols, when there are two at the same heat flux, represent tar yield for 2 different particle densities. It can be seen that a 0.3 g/cc density change has little effect on tar yield. The trend lines result from regression of all the data to a single set of parameters for Eq. 1. The average prediction error as approximated by the standard error of the residuals is 2%, and the standard deviation of replicate runs is the same. In Fig. 2, the synergy, or interaction of particle size and heat flux can be clearly seen. The reduction in tar for an increase in heating rate, as characterized by the slope of the trend lines at any point, increases as the particle thickness increases. The thickest particle pyrolyzed at the lowest heat flux produces over 65% tar, and it decreases to 20% at the maximum intensity investigated. This is consistent with the extensive tar cracking that likely occurs near the particle surface char zone where high temperatures prevail

for severe heating. Note that all dry particles heated at the intermediate heat flux result in approximately 25%-35% tar.

The pyrolytic tar produced from a wet wood particle is presented in Fig. 3 as a function of both initial moisture content (abscissa) and heating intensity for the thickest particle size used in this study, 1.5 cm. The prediction error and the experimental error in the measured tar from wet particle pyrolysis is about 5%. Note that moisture causes the optimum tar conditions to occur at 4 cal/cm²-s, rather than the 2 cal/cm²-s for dry particles, consistent with the lower particle temperature expected when water is present. Overall, the level of tar produced is considerably higher, 50-70%, than for dry wood particles. Hydrogen is measured in the gases, as well.

In Fig. 4, a composition profile of some components of both tar and gas is presented. Changes in this profile simply highlight changes in composition as process conditions change. The ordinate is the weight fraction of the reacted portion of the 1 cm particle data used in this figure. Thus all components plotted are each less than 2% of the moist wood particle that was pyrolyzed. The error as estimated from replicated determinations is about 0.5%. The high molecular weight species composition appears to vary little as particle temperature is manipulated by changing both moisture and heating intensity of the pyrolysis. However, the low molecular weight tar compounds are in greater concentration for mild intensity heating (2 cal/cm²-s) than for a greater heating rate which appears to favor the hydrocarbon gases and hydrogen. Although the composition differences are nearly within the experimental error, moisture appears to slightly enhance the production of methanol and acetic acid for these experiments (1 cm particle).

CONCLUSIONS

Data has been presented which suggests that moisture can enhance the production of tar from the pyrolysis of large wood particles using conditions that occur in a large scale reactor where the heat flux a particle experiences is quite constant. The most favorable conditions result in about 70% of the reacted biomass becoming tar. If one assumes that the mass balance discrepancy results from tar condensing on reactor surfaces, this is a conservative estimate.

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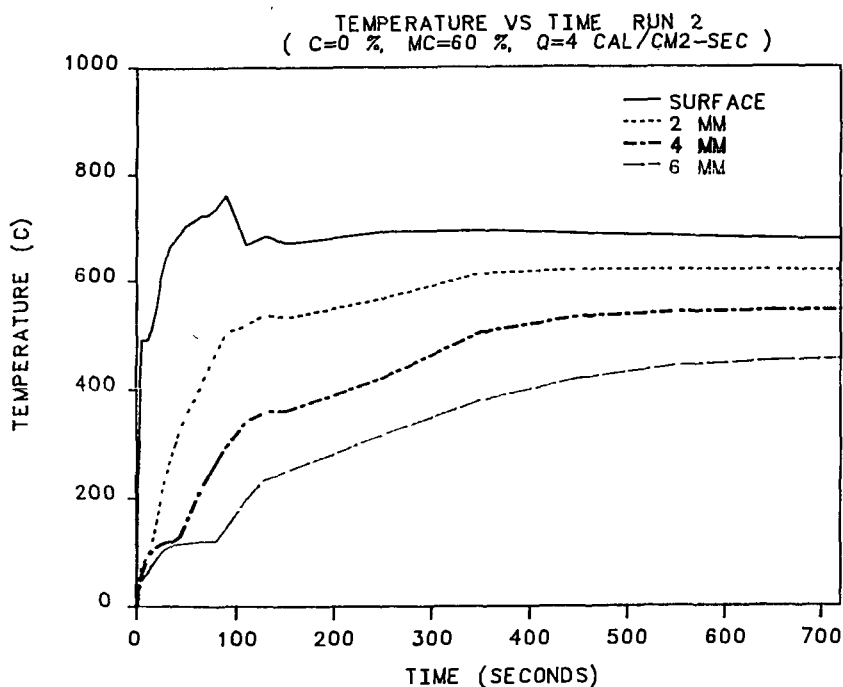


Fig. 1 - Temperature histories at 4 positions in a 1 cm thick wood particle pyrolyzed with an applied heat flux of 4 cal/cm²-s.

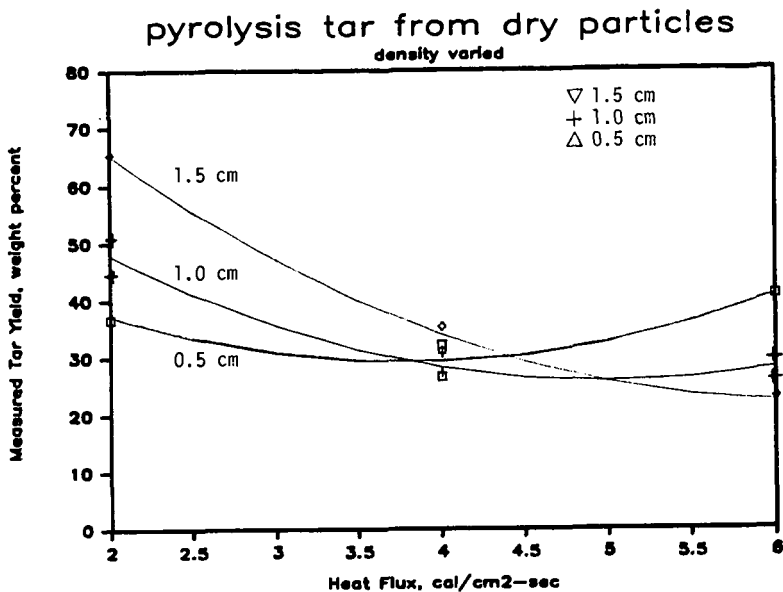


Fig. 2 - Weight fraction tar yield for the pyrolysis of dry wood particles at varying surface heat fluxes for three thicknesses; trend lines are least square fits and symbols are some of the experimental data.

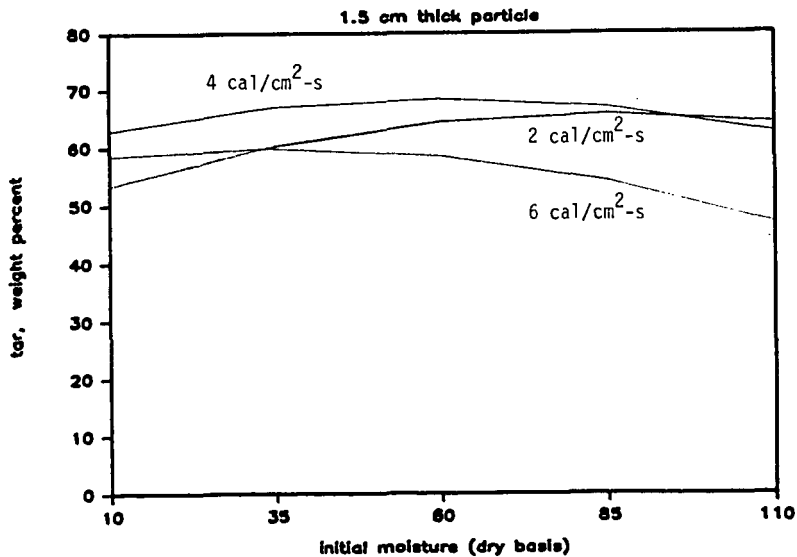


Fig. 3 - Measured weight fraction tar produced from a 1.5 cm thick wood particle as a function of moisture content for 3 different heating rates.

pyrolysis product profile

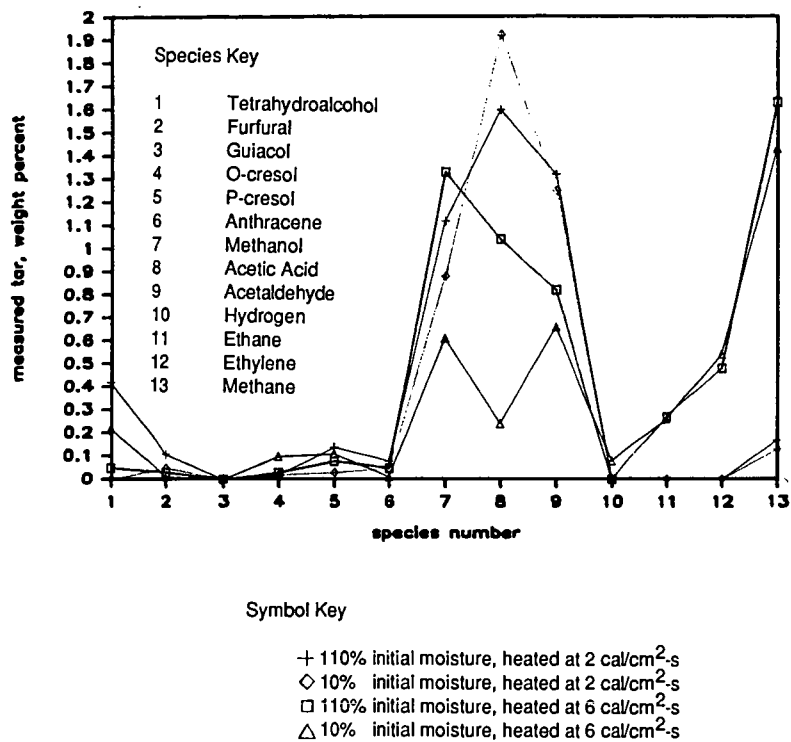


Fig. 4 - Product composition profile for two moisture content 1 cm thick particles heated at two heating rates.